(12) # EUROPEAN PATENT APPLICATION

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(54) Pyridinethione salts, a process for making thereof and hair care compositions containing them.

(57) Heavy metal salts of 1-hydroxy-2-pyridinethione in the form of crystals having defined shape and size, are useful in shampoos, creme rinses and other hair care compositions to deliver antidandruff benefits while not detracting as much as previous pyridinethione salts from the compositions' aesthetics. Hair care compositions containing such salts are also included.

A process for producing heavy metal 1-hydroxy-2-pyridinethione salts comprises reacting a water soluble salt of the desired metal with 1-hydroxy-2-pyridinethione or with a water-soluble salt of the pyridinethione in an aqueous surfactant medium.

EP 0 034 385 A2

COMPLETE DOCUMENT

PYRIDINETHIONE SALTS, A PROCESS FOR MAKING
THEREOF AND HAIR CARE COMPOSITIONS CONTAINING
THEM

The present invention relates to heavy metal
salts of 1-hydroxy-2-pyridinethione which are in
crystalline form and possess a geometry and particle
size which make the crystals more compatible in a
composition matrix, to a process for producing the
metal salts of 1-hydroxy-2-pyridinethione, and to
hair care compositions containing them.

Pyridinethione salts are old as shown by US
Patent 2,809,971, October 15, 1957 to Bernstein et al.
Other patents disclosing similar compounds and processes
for making them include US Patent 2,786,847, March 26,
1957 to Cislak and US Patents 3,583,999, June 8, 1971;
3,590,035, June 29, 1971; and 3,773,770, November 20,
1973 all to Damico.

The use of pyridinethione salts as antidandruff
agents in shampoos and hair rinses is well known. US
Patent 3,236,733, Feburary 22, 1966 to Karsten et al
discloses detergent compositions containing such salts.
Barnett, B L et al, "Structural Characterization of
Bis(N-oxypyridine-2-thionato)Zinc(II)," _Inorganic
Chemistry_, _16_, 1834, /1977/ discloses recrystallizing
zinc pyridinethione crystals from chloroform or dimethyl
sulfoxide. Other references which disclose pyridine-
thione salts are US Patent 2,809,971, October 15, 1957

to Bernstein et al; U.S. Patent 3,723,325, March 27, 1973
to Parran; U.S. Patent 3,753,916, August 21, 1973 to
Parran; U.S. Patent 3,761,417, September 25, 1973 to
Parran; and U.S. Patent 3,761,418, September 24, 1973
5   to Parran.

While it is known to use pyridinethione salts in
hair care compositions the prior art does not indicate
whether the salts are compatible with all components
which may be present in a composition. Included among
10   components which may be present in shampoos and other
hair care compositions are those which make the composi-
tions more aesthetically appealing. Aesthetics are
important in encouraging a consumer to purchase a product
as well as continue using the product after purchase.

15   One aesthetic characteristic which has found wide
acceptance is pearlescence. This is quite often achieved
through the use of material such as ethylene glycol
distearate. The pyridinethione salt materials available
up to this time have substantially interfered with the
20   ability of pearlescent material to deliver acceptable
pearlescence. This has been due, in all likelihood, to
the materials being in the shape of cubes and rods and of
small size. The recrystallized material of Barnett et al
supra, while allowing pearlescence, has been found to be
25   less acceptable than the crystals of the present invention
in finished compositions.

Furthermore, while the prior art discloses pyridine-
thione salts and processes for making such salts, it does
not suggest forming the salts in an aqueous surfactant
30   medium. Furthermore, there is no suggestion that the
crystals formed in such a medium would have superior
aesthetic properties and be more compatible in a
composition.

It is therefore an object of the present invention to provide pyridinethione salt crystals which interfere less with the pearlescent material than do prior art materials.

It is another object of the present invention to provide antidandruff compositions containing such crystals.

It is yet another object of the present invention to provide an improved method for making pyridinethione salt crystals.

These and other objects will become obvious from the detailed description which follows.

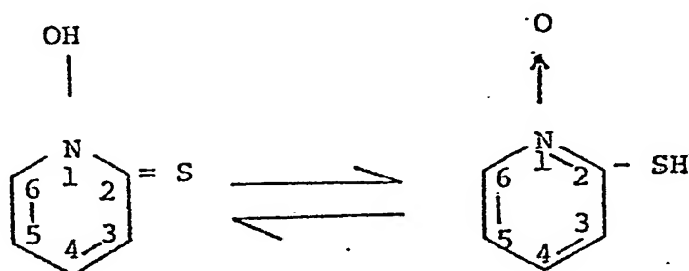### Disclosure of the Invention

The present invention relates to pyridinethione salt crystals which are predominantly flat platelets having a mean sphericity less than about 0.65 and a median particle size of at least about 2μ diameter, expressed as the equivalent diameter of a sphere of equal volume. Compositions containing such crystals are also part of the present invention.

The present invention further relates to the formation of heavy metal pyridinethione salt crystals by reacting pyridinethione or a water soluble pyridinethione salt with a water soluble salt of the desired heavy metal in an aqueous surfactant medium. The concentration of surfactant is not critical but is preferably from about 1% to about 24%, more preferably from about 1% to about 8%. The reaction temperature is at least about 20°C., preferably from about 60°C. to about 100°C. The crystals may be separated from the reaction medium after formation for use in a particular formulation not containing the surfactant used in the reaction. Alternatively, if desired, the crystals may be left in the reaction medium for incorporation into a final composition.

Detailed Description of the Invention

Pyridinethione Salt Crystals

The present invention is concerned with heavy metal
salts of 1-hydroxy-2-pyridinethione which has the follow-
ing structural formula in tautomeric form, the sulfur
being attached to the No. 2 position in the pyridine ring.

The heavy metal salts represent substitution of the
metal cation for the hydrogen of one of the tautomeric
forms. Depending, of course, on the valence of the metal
involved there may be more than one of the pyridinethione
rings in the compound. Suitable heavy metals include zinc,
tin, cadmium, magnesium, aluminum and zirconium.

The present pyridinethione salt crystals are pre-
dominantly flat platelets which have a mean sphericity
less than about 0.65, preferably between about 0.20 and about
0.65 and a median particle size of at least about 2μ
diameter, expressed as the median equivalent diameter of
a sphere of equal volume. It is preferred that the mean
particle size be not greater than about 15μ, measured
on the same basis. The median diameters are on a mass
basis with 50% of the mass of particles falling on
either side of the value given.

The diameter of a sphere of equivalent volume
for a particle can be determined by a variety of sedi-

mentation techniques which are based on Stokes' Law for the settling velocity of a particle in a fluid. Such techniques are described in Stockham, J.D. and Fochtman, E.G., _Particle Size Analysis_, Ann Arbor Science, 1978, incorporated herein by reference. An approach for determining the median equivalent spherical diameter based on volume, $\bar{d}_v$, is shown in Example II.

The sphericity of a particle is also described by Stockham and Fochtman at page 113 as

$$\psi = \left(\frac{d_v}{d_s}\right)^2$$

where d_v is the diameter of a sphere of equivalent volume, supra, and d_s is the diameter of a sphere of equivalent area. In the present invention the mean sphericity =

$$\left(\frac{\bar{d}_v}{\bar{d}_s}\right)^2 \quad \text{or}$$

surface area of spheres having equivalent volume distribution divided by the actual surface area of particles as measured

A technique for determining actual surface area is shown in the examples using the BET technique described by Stockham and Fochtman at page 122.

Compositions Containing the Pyridinethione Metal Salts

The pyridinethione metal salts of the present invention are useful in a variety of hair care compositions as antidandruff aids. The salts are generally present at a level of from about 0.2% to about 4.0%, preferably from about .3% to about 2.0%, even more preferably from about 1% to about 2% in some compositions. Included among the hair care compositions are shampoos, creme rinses, hair tonics and many others. Shampoos are the preferred compositions and components generally found in such compositions are given below.

Surfactant

One essential component of the antidandruff shampoos herein is a surfactant. The term "surfactant" as used herein is intended to denote soap and nonsoap surfactants.
5 The surfactant component comprises from about 10% to about 50% by weight of the composition, preferably 10% to about 20%.

Any nonsoap surfactant is suitable for use including anionic, nonionic, amphoteric and zwitterionic types. Cationic surfactants may also be used, but these are not
10 preferred in the shampoos of the present invention due to their irritation potential.

Examples of suitable soaps are the sodium, potassium, ammonium and alkanol ammonium salts of higher fatty acids (those having 10-20 carbon atoms). Anionic
15 nonsoap surfactants can be exemplified by the alkali metal salts of organic sulfuric reaction products having in their molecular structure an alkyl radical containing from 8 - 22 carbon atoms and a sulfonic acid or sulfuric acid ester radical (included in the term alkyl is the alkyl
20 portion of higher acyl radicals). Preferred are the sodium, ammonium, potassium or triethanolamine alkyl sulfates, especially those obtained by sulfating the higher alcohols (C_8 - C_{18} carbon atoms), sodium coconut oil fatty acid monoglyceride sulfates and sulfonates; sodium or potas-
25 sium salts of sulfuric acid esters of the reaction product of 1 mole of a higher fatty alcohol (e.g., tallow or coconut oil alcohols) and 1 to 12 moles of ethylene oxide; sodium or potassium salts of alkyl phenol ethylene oxide ether sulfate with 1 to 10 units of ethylene oxide
30 per molecule and in which the alkyl radicals contain from 8 to 12 carbon atoms, sodium alkyl glyceryl ether sulfonates; the reaction product of fatty acids having from 10 to 22 carbon atoms esterified with isethionic acid and neutralized with sodium hydroxide; water soluble
35 salts of condensation products of fatty acids with sarcosine; and other known in the art.

Nonionic surfactants can be broadly defined as compounds produced by the condensation of alkylene oxide groups (hydrophilic in nature) with an organic hydrophobic compound, which may be aliphatic or alkyl aromatic in nature. Examples of preferred classes of nonionic surfactants are:

1. The polyethylene oxide condensates of alkyl phenols, e.g., the condensation products of alkyl phenols having an alkyl group containing from about 6 to 12 carbon atoms in either a straight chain or branched chain configuration, with ethylene oxide, the said ethylene oxide being present in amounts equal to 10 to 60 moles of ethylene oxide per mole of alkyl phenol. The alkyl substituent in such compounds may be derived from polymerized propylene, diisobutylene, octane, or nonane, for example.

2. Those derived from the condensation of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylene diamine products which may be varied in composition depending upon the balance between the hydrophobic and hydrophilic elements which is desired. For example, compounds containing from about 40% to about 80% polyoxyethylene by weight and having a molecular weight of from about 5,000 to about 11,000 resulting from the reaction of ethylene oxide groups with a hydrophobic base constituted of the reaction product of ethylene diamine and excess propylene oxide, said base having a molecular weight of the order of 2,500 to 3,000, are satisfactory.

3. The condensation product of aliphatic alcohols having from 8 to 18 carbon atoms, in either straight chain or branched chain configuration, with ethylene oxide, e.g., a coconut alcohol ethylene oxide condensate having from 10 to 30 moles of ethylene oxide per mole of coconut alcohol, the coconut alcohol fraction having from 10 to 14 carbon atoms.

4. Long chain tertiary amine oxides corresponding to the following general formula:

$$R_1R_2R_3N \longrightarrow O$$
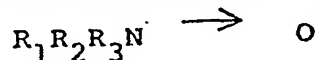
wherein R_1 contains an alkyl, alkenyl or monohydroxy alkyl radical of from about 8 to about 18 carbon atoms, from 0 to about 10 ethylene oxide moieties, and from 0 to 1 glyceryl moiety, and R_2 and R_3 contain from 1 to about 3 carbon atoms and from 0 to about 1 hydroxy group, e.g., methyl, ethyl, propyl, hydroxy ethyl, or hydroxy propyl radicals. The arrow in the formula is a conventional representation of a semipolar bond. Examples of amine oxides suitable for use in this invention include dimethyldodecylamine oxide, oleyldi(2-hydroxyethyl)amine oxide, dimethyloctylamine oxide, dimethyldecylamine oxide, dimethyltetradecylamine oxide, 3,6,9-trioxaheptadecyldiethylamine oxide, di(2-hydroxyethyl)-tetradecylamine oxide, 2-dodecoxyethyldimethylamine oxide, 3-dodexocy-2-hydroxypropyldi(3-hydroxypropyl)amine oxide, dimethylhexadecylamine oxide.

5. Long chain tertiary phosphine oxides corresponding to the following general formula:

$$RR'R''P \longrightarrow O$$
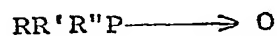
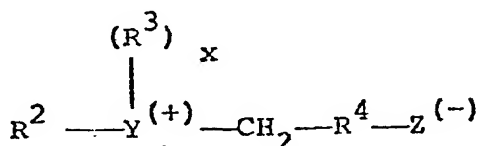wherein R contains an alkyl, alkenyl or monohydroxyalkyl radical ranging from 8 to 18 carbon atoms in chain length, from 0 to about 10 ethylene oxide moieties and from 0 to 1 glyceryl moiety and R' and R" are each alkyl or monohydroxyalkyl groups containing from 1 to 3 carbon atoms. The arrow in the formula is a conventional representation of a semipolar bond. Examples of suitable phosphine oxides are:

dodecyldimethylphosphine oxide,
tetradecyldimethylphosphine oxide,
tetradecylmethylethylphosphine oxide,
3,6,9-trioxaoctadecyldimethylphosphine oxide,
cetyldimethylphosphine oxide,
3-dodecoxy-2-hydroxypropyldi(2-hydroxyethyl)phosphine oxide,
stearyldimethylphosphine oxide,
cetylethylpropylphosphine oxide,
oleyldiethylphosphine oxide,
dodecyldiethylphosphine oxide,
tetradecyldiethylphosphine oxide,
dodecyldipropylphosphine oxide,
dodecyldi(hydroxymethyl)phosphine oxide,
dodecyldi(2-hydroxyethyl)phosphine oxide,
tetradecylmethyl-2-hydroxypropylphosphine oxide,
oleyldimethylphosphine oxide,
2-hydroxydodecyldimethylphosphine oxide.

6. Long chain dialkyl sulfoxides containing one
short chain alkyl or hydroxy alkyl radical of 1 to about
3 carbon atoms (usually methyl) and one long hydrophobic
chain which contain alkyl, alkenyl, hydroxy alkyl, or
keto alkyl radicals containing from about 8 to about 20
carbon atoms, from 0 to about 10 ethylene oxide moieties
and from 0 to 1 glyceryl moiety. Examples include:

octadecyl methyl sulfoxide,
2-ketotridecyl methyl sulfoxide,
3,6,9-trioxaoctadecyl 2-hydroxyethyl sulfoxide,
dodecyl methyl sulfoxide,
oleyl 3-hydroxypropyl sulfoxide,
tetradecyl methyl sulfoxide,
3-methoxytridecyl methyl sulfoxide,
3-hydroxytridecyl methyl sulfoxide,
3-hydroxy-4-dodecoxybutyl methyl sulfoxide.

Zwitterionic surfactants can be exemplified by those which can be broadly described as derivatives of aliphatic quaternary ammonium, phosphonium, and sulfonium compounds, in which the aliphatic radicals can be straight chain or branched, and wherein one of the aliphatic substituents contains from about 8 to 18 carbon atoms and one contains an anionic water-solubilizing group, e.g., carboxy, sulfonate, sulfate, phosphate, or phosphonate. A general formula for these compounds is:

$$R^2 —Y^{(+)}\overset{\overset{\displaystyle (R^3)}{|}}{}\hspace{-0.5em}{}_x —CH_2—R^4—Z^{(-)}$$

wherein R^2 contains an alkyl, alkenyl, or hydroxy alkyl radical of from about 8 to about 18 carbon atoms, from 0 to about 10 ethylene oxide moieties and from 0 to 1 glyceryl moiety; Y is selected from the group consisting of nitrogen, phosphorus, and sulfur atoms; R^3 is an alkyl or monohydroxyalkyl group containing 1 to about 3 carbon atoms; X is 1 when Y is a sulfur atom and 2 when Y is a nitrogen or phosphorus atom; R^4 is an alkylene or hydroxy-alkylene of from 1 to about 4 carbon atoms and Z is a radical selected from the group consisting of carboxylate, sulfonate, sulfate, phosphonate, and phosphate groups.

Examples include:

4-[N,N-di(2-hydroxyethyl)-N-octadecylammonio]-butane-1-carboxylate;

5-[S-3-hydroxypropyl-S-hexadecylsulfonio]-3-hydroxypentane-1-sulfate;

3-[P,P-diethyl-P-3,6,9-trioxatetradexocylphosphonio]-2-hydroxypropane-1-phosphate;

3-[N,N-dipropyl-N-3-dodecoxy-2-hydroxypropylammonio]-propane-1-phosphonate;

3-(N,N-dimethyl-N-hexadecylammonio)propane-1-sulfonate;

3-(N,N-dimethyl-N-hexadecylammonio)-2-hydroxypropane-1-sulfonate;

4-[N,N-di(2-hydroxyethyl)-N-(2-hydroxydodecyl)ammonio]-butane-1-carboxylate;

3-[S-ethyl-S-(3-dodecoxy-2-hydroxypropyl)sulfonio]-propane-1-phosphate;

3-(P,P-dimethyl-P-dodecylphosphonio)-propane-1-phosphonate; and

5-[N,N-di(3-hydroxypropyl)-N-hexadecylammonio]-2-hydroxy-pentane-1-sulfate.

Examples of amphoteric surfactants which can be used in the compositions of the present invention are those which can be broadly described as derivatives of aliphatic secondary and tertiary amines in which the aliphatic radical can be straight chain or branched and wherein one of the aliphatic substituents contains from about 8 to about 18 carbon atoms and one contains an anionic water solubilizing group, e.g., carboxy, sulfonate, sulfate, phosphate, or phosphonate. Examples of compounds falling within this definition are sodium 3-dodecylaminopropionate, sodium 3-dodecylaminopropane sulfonate, N-alkyltaurines such as the one prepared by reacting dodecylamine with sodium isethionate according to the teaching of U.S. Patent No. 2,658,072, N-higher alkyl aspartic acids such as those produced according to the teaching of U.S. Patent No. 2,438,091, and the products sold under the trade name "Miranol" and described in U.S. Patent No. 2,528,378.

Many cationic surfactants are known to the art. By way of example, the following may be mentioned:

dodecyltrimethylammonium chloride;

nonylbenzylethyldimethylammonium nitrate;

tetradecylpyridinium bromide;

laurylpyridinium chloride;

cetylpyridinium chloride;

laurylpyridinium chloride;

laurylisoquinolium bromide;

ditallow(hydrogenated)dimethyl ammonium chloride

dilauryldimethylammonium chloride; and

stearalkonium chloride.

Many additional nonsoap surfactants are described
in McCUTCHEON'S, DETERGENTS AND EMULSIFIERS, 1979 ANNUAL,
published by Allured Publishing Corporation, which is
incorporated herein by reference.

The above-mentioned surfactants can be used alone
or in combination in the shampoo compositions of the
present invention.

Pearlescent Material

Another desirable component of the shampoos herein
is a pearlescent material. Such materials are well known
in the art and include bismuth oxychloride, stearic
monoethanolamide, ethylene glycol monostearate or dis-
tearate, guanine and titanium dioxide coated mica.
A pearlescent material is generally present at a level
of from about .1% to about 6%, preferably from about
.5% to about 5%.

Aqueous Carrier

The shampoos herein are preferably in the form of
liquids or creams in which water is the principal diluent.
The level of water in the compositions is typically from
about 35% to about 90% by weight.

Optional Components

The antidandruff shampoos herein can contain a variety of non-essential optional ingredients suitable for rendering such compositions more stable and desirable. Such conventional optional ingredients are well known to those skilled in the art, e.g., preservatives such as benzyl alcohol, methyl paraben, propyl paraben and imidazolidinyl urea; thickeners and viscosity modifiers such as coconut ethanol amide, sodium chloride, sodium sulfate, carboxymethylcellulose, methylcellulose, polyvinyl alcohol, and ethyl alcohol; pH adjusting agents such as citric acid, succinic acid, phosphoric acid, sodium hydroxide, sodium carbonate, etc.; suspending agents such as magnesium/aluminum silicate; perfumes, dyes; and, sequestering agents such as disodium ethylenediamine tetraacetate.

Minor ingredients such as perfumes, dyes and coloring agents can also be added to the instant compositions to improve their consumer acceptability. If present, such agents generally comprise from about 0.1% to 2.0% by weight of the composition. The pH of the shampoos herein is generally from about 3 to about 9.

Other Hair Care Compositions

Creme rinses, hair tonics and other hair care compositions as well as shampoos may contain the pyridinethione salts of the present invention. These compositions may contain a variety of other components including some of those described supra for shampoos. Creme rinses generally contain a cationic surfactant similar to those described supra, particularly stearalkonium chloride and ditallow dimethyl ammonium chloride at a level of from about .1% to about 5%, preferably from about .5% to about 2%.

METHOD OF MANUFACTURE

The hair care compositions containing the pyridine-thione salt crystals may be made using techniques well known in the art.

5   The heavy metal pyridinethione salt crystals used in the compositions of this invention are prepared by a process which involves the steps enumerated herein above. The reactants can be handled in a wide variety of ways. For example, the water soluble salt of the desired heavy
10   metal may be combined with part of the surfactant and water while the remainder of the water and surfactant are combined with pyridinethione or a water soluble pyridine-thione salt. The two mixtures are then combined. Alternatively, all of the surfactant may be combined with
15   either material or put into a third container into which the materials are then placed. All of these approaches are satisfactory since the crystals form almost instan-taneously regardless of the approach used.

The various reaction materials are discussed in
20   detail below.

Pyridinethione and Water Soluble Pyridinethione Salts

Pyridinethione as the term is used herein is 1-hydroxy-2-pyridinethione which has the following structural formula in tautomeric form, the sulfur being
25   attached to the No. 2 position in the pyridine ring.
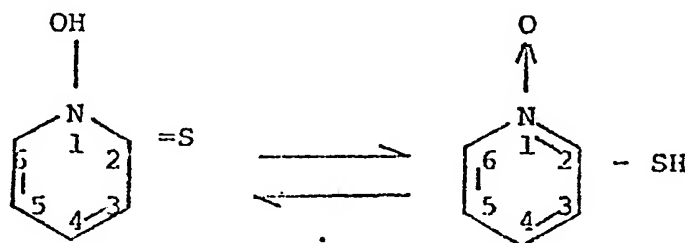
The water soluble salts represent substitution of the
metal cation for the hydrogen of one of the tautomeric
forms. The preferred salts are those involving ammonium
or alkali metals. Most preferred is the sodium salt.

. 5   The amount of 1-hydroxy-2-pyridinethione or water
soluble salt can vary over a wide range (the level
only dependent on the quantity of material desired). A
preferred level is from about 8% to about 16% of the
total reaction system.

10   Water Soluble Salt Of A Heavy Metal

        Suitable heavy metal compound reactants include salts
in which the heavy metal may be, among others, zinc, tin,
magnesium, aluminum, cadmium or zirconium. The compounds
may be nitrates, acetates, sulfates or halogens. The pre-
15 ferred salts are sulfates and zinc sulfate is the most
preferred. The amount of soluble heavy metal salt used
is not critical so long as the amount is sufficient to
form the desired pyridinethione salt. The amount used
therefore is generally an amount sufficient to provide a
20 stoichiometric excess. An excess of about 5% is an example
of a suitable excess amount.

Surfactant

        Another necessary component in the process of the
present invention is a surfactant. The term "surfactant"
25 as used herein is intended to denote soap and nonsoap
surfactants. Any nonsoap surfactant is suitable for
use including anionic, nonionic, amphoteric, cationic
and zwitterionic types. The surfactant should be solu-
ble in water at the temperature of the reaction.

Examples of surfactants suitable for use in the
process of this invention are the same surfactants which
are described herein above as examples of surfactants
suitable for use in the compositions of the invention
5   herein. These surfactants can be used alone or in com-
bination in the process herein. As noted above in the
description of the process of this invention, surfactant
is preferably used in the process herein at a concen-
tration of from about 1% to about 24%, more preferably
10   from about 1% to about 8%, and surfactant used in the
process herein should be soluble in water at the tempera-
ture of the reaction.

Reaction Temperature

The reaction temperature should be above about 20°C.,
15   preferably from about 60°C. to about 100°C. The tempera-
ture can be achieved and maintained through the use of
any of the techniques well known in the art.

Reactant Medium

The process of the present invention is carried out
20   in an aqueous medium wherein water is the major diluent.

INDUSTRIAL APPLICABILITY

The pyridinethione salts and compositions containing
them are useful in combatting dandruff. Such composi-
tions are used in a conventional manner.

25   ·   The following Examples further describe and demon-
strate the preferred embodiments within the scope of the
present invention. The Examples are given solely for the
purpose of illustration and are not to be construed as

limitations of the present invention as many variations
thereof are possible without departing from its spirit
and scope. Unless otherwise indicated, all percentages
herein are by weight.

EXAMPLE I

Zinc pyridinethione salt crystals of the present
invention were made using the following procedure.

A first mixture was prepared by combining 14.7
parts of zinc sulfate, 21.7 parts of a 29% aqueous
5   solution of sodium alkyl sulfate and 8.6 parts of water
in a mix tank. This mixture was heated to 95°C.

A second mixture was prepared by combining 35
parts of a 40% aqueous solution of sodium pyridinethione
with 20 parts of a 29% aqueous solution of sodium
10 alkyl sulfate in a mix tank. This second mixture was
also heated to 95°C.

The first mixture was added to the second mixture
resulting in the formation of zinc pyridinethione
crystals which were washed and collected.

15   The total batch size, the combined mixtures,
was 2500 grams.

EXAMPLE II

The crystals of zinc pyridinethione made according to Example I were evaluated to determine their particle size and sphericity.

The median equivalent spherical diameter based
5 on volume (particle size) was determined by means of a SediGraph 500 D Particle Size Analyzer supplied by Micrometrics Instrument Corporation.

The SediGraph 5000 D determines, by means of X-ray absorption, the concentration of particles remaining
10 at decreasing sedimentation depths as a function of time. Stokes' Law relates the measured equilibrium velocity of a particle falling through à viscous medium to its equivalent spherical diameter (ESD).

$$15 \qquad ESD = \left[\frac{18 \cdot \eta \cdot v}{(\rho - \rho_o)g} \right]^{1/2}$$

η = liquid viscosity

v = equilibrium velocity

ρ_o = liquid density

g = gravitational acceleration

20 ρ = particle density

v is determined from the Sedigraph while the other variables are available from reference sources or obtained experimentally. In the present analysis water was the liquid and the liquid viscosity was 0.76 cp.

The density of ZPT particles is known to be about
1.81 g/cc, (Barnett, B.L., et al, "Structural
Characterization of Bis-(N-oxypyridine-2-thionato) Zinc
(II)", Inorganic Chemistry 16, 1934, [1977]), incorpor-
ated herein by reference.

5   The median equivalent spherical diameter based on
volume ($\bar{d}_v$) of the crystals using Stokes' Law was deter-
mined to be 5.4µ.

       This median equivalent spherical diameter was taken
from the mass distribution of particles described in
10 1. below. The determination of a specific surface area
based on equivalent spherical diameters was as follows:

       1.   A cumulative mass distribution of equivalent
spherical diameters in µm was obtained using the SediGraph
instrument described previously. The rate for the in-
15 strument was 866 and the starting diameter of 100µm.

       2.   The cumulative mass distribution was divided
into equal logarithmic intervals in µm. The sizes of the
intervals are shown in the following table.

       3.   The cumulative mass distribution at each equal
20 logarithmic interval was determined.

       4.   The diameter at the centerpoint of each interval
was determined.

       5.   The value of the cumulative mass percent dis-
tribution at the centerpoints of the intervals was de-
25 termined.

       6.   The value of the differential mass percent
distribution was then determined.

7. The amount of material for each interval was determined, assuming that there was a total of one gram which was evaluated. These values are the values in 6, above, divided by 100.

5 8. The assumed spherical particle surface area of the material contained in each interval was calculated using diameters equal to the centerpoints of the intervals. Therefore, the calculation for a particular interval, i, is

10

$$A_i = \frac{\text{(Mass contained in interval i)}}{\text{(Mass of sphere with diameter } d_i)} \text{x}$$

(Surface area of sphere with diameter d_i)

$$A_i = \frac{\text{Mass contained in interval i}}{\rho \, 4/3 \, \pi \left(\frac{d_i}{2}\right)^3} \left(d_i\right)^2 \pi = \frac{6}{\rho} \frac{\text{mass}}{d_i}$$

15 $A = \Sigma_i A_i$ = Surface area/g assuming spheres

All of the above data are shown in the following table. The numerical column headings correspond to the numbers above.

	2	3	4	5	6	7	8
	1.59	0.					
			1.78	0.5	0.5	0.005	0.009
	2.00	1.0					
5			2.28	2.5	2.0	0.020	0.029
	2.52	4.0					
			2.87	7.0	4.5	0.045	0.052
	3.17	10.0					
			3.59	16.0	9.0	0.090	0.083
10	4.00	22.0					
			4.52	32.0	16.0	0.160	0.118
	5.04	42.0					
			5.70	55.0	23.0	0.230	0.134
	6.35	68.0					
15			7.18	76.0	21.0	0.210	0.097
	8.00	84.0					
			9.04	88.5	12.5	0.125	0.046
	10.08	93.0					
			11.4	95.0	6.5	0.065	0.019
20	12.7	97.0					
			14.4	98.0	3.0	0.030	0.007
	16.0	99.0					
			18.1	99.5	1.5	0.015	0.003
	20.2	100.0					
25			22.8	100.0	0.5	0.005	0.001
	25.4	100.0					
				TOTAL - 100.0		1.000g	0.598 m²/g

The specific surface area for the crystals was determined by means of a B.E.T. surface area analysis using nitrogen gas. The B.E.T. analysis showed the crystals to have a specific surface area of 2.39 m^2/g.

5   The sphericity was then determined as follows:

$$\psi = \frac{\text{area per g calculated for assumed spherical distribution}}{\text{area per g from B.E.T. measurement}}$$

$$\psi = \frac{0.598}{2.39} = 0.25$$

EXAMPLE III

A shampoo composition having the following formula
was prepared.

Component	Level
Ammonium Alkyl Sulfate (29% Aqueous solution)	55.25%
Zinc Pyridinethione Crystals of Example I	2.0
Coconut Monoethanolamide	3.0
Ethylene Glycol Distearate	5.0
Sodium Citrate	0.5
Citric Acid	0.2
Color Solution	0.1
Perfume	0.5
Water	q.s.100.00%

The pearlescence of this composition was better
than an identical composition containing prior art zinc
pyridinethione particles having a mean sphericity of
about 0.75 and a mean equivalent spherical diameter
based on volume of about 1.25μ.

EXAMPLE IV

The following shampoo is prepared.

Component	Level
Triethanolamine Alkyl Sulfate (35% Aqueous Solution)	50.0%
Triethanolamine	3.0
Coconut Monoethanolamide	2.0
Magnesium/Aluminum Silicate	0.5
Hydroxy Methyl Cellulose	0.6
Zinc Pyridinethione crystals of Example I	2.0
Color Solution	0.1
Perfume	0.3
Water	q.s.100.0%

EXAMPLE V

The following cream shampoo is prepared.

Component		Level
Sodium Alkyl Glyceryl Sulfonate		60.0%
5 Sodium Chloride		5.0
Sodium N-Lauroyl Sarcosinate		12.0
N-Cocoyl Sarcosine Acid		1.0
Lauric Dethanolamide		2.0
Zinc Pyridinethione of Example I		2.0
10 Perfume		0.5
Color Solution		0.12
Water	q.s.	100.00%

EXAMPLE VI

. The following creme rinse is prepared.

Component		Level
Stearalkonium Chloride		0.75%
5 Stearyl Alcohol		0.5
Zinc Pyridinethione of Example I		0.3
Cetyl Alcohol		0.5
Polyoxyethylene (2) Cetyl Ether		0.8
Sodium Chloride		0.25
10 Color Solution		0.2
Perfume .		0.25
Water	q.s.	100.00%

EXAMPLE VII

Zinc pyridinethione salt crystals were made using the following process of the present invention.

A first mixture was prepared by combining 7.3
5 parts of a 28% aqueous solution of ammonium alkyl sulfate, 2 parts of zinc sulfate and 40.7 parts of water in one mix tank. The mixture was heated to 80°C.

A second mixture was prepared by combining 7.3 parts of a 28% aqueous solution of ammonium alkyl sulfate, 5
10 parts of a 40% aqueous solution of sodium pyridinethione and 37.7 parts of water in another mix tank. This mixture was also heated to 80°C.

The first and second mixtures were metered into a third tank at the rate of 1 kg./min. The resulting
15 zinc pyridinethione crystals were washed and stored.

Claims

1.   A heavy metal salt of 1-hydroxy-2-pyridinethione
characterised by being in the form of crystals having
a mean sphericity of less than 0.65 and a median
5   equivalent spherical diameter based on volume of at
least 2 μm but less than 15 μm.

2.   A pyridinethione salt according to Claim 1
characterised in that the heavy metal is selected
from the group consisting of zinc, tin, magnesium,
10   aluminum, cadmium and zirconium.

3.   A pyridinethione salt according to Claim 1 or 2
characterised in that the mean sphericity is from
0.20 to 0.65.

4.   A hair care composition characterised in that it
15   contains from 0.2% to 4.0% of a pyridinethione salt
according to any of Claims 1 to 3.

5.   A hair care composition according to Claim 4
characterised by being in the form of a shampoo
which additionally contains from 10% to 50% of a
20   surfactant.

6.   A shampoo according to Claim 5 characterised in
that it additionally contains from 0.1% to 6.0%
of a pearlescent material.

7.   A hair care composition according to Claim 4
25   characterised by being in the form of a creme rinse
which additionally contains from 0.1% to 5.0% of a
cationic surfactant and from 95% to 99% water.

8.   A process for making a heavy metal pyridinethione
salt characterised by reacting 1-hydroxy-2-pyridineth-
30   ione or a water soluble salt thereof with a water
soluble heavy metal salt in an aqueous surfactant
medium, wherein the reaction temperature is at least
20°C.

9.   A process according to Claim 8 characterised in
35   that the pyridinethione compound is an alkali metal
pyridinethione salt and the concentration of

surfactant in the total reaction mixture is from
1% to 24%.

10. A process according to Claim 8 or 9 characterised
in that the heavy metal salt is selected from the

5   group consisting of zinc, tin, magnesium, aluminum,
cadmium and zirconium salts and is present in an
amount sufficient to provide a stoichiometric excess.

11. A process according to any of Claims 8 to 10
characterised by reacting sodium 1-hydroxy-2-pyridin-

10   ethione with a water-soluble zinc salt in an aqueous
anionic surfactant medium at a temperature in the
range from 60°C to 100°C, wherein the concentration
of surfactant in the total reaction mixture is from
1% to 8%.